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16. ABSTRACT The paper describes a determination of the basic properties of laboratory quantities of potential alternative compounds which may be used to replace chlorofluorocarbons (CFCs) and halons listed in the "Montreal Protocol for Substances that Deplete the Ozone Layer." The property testing currently posed for investigation was designed to assist in the determination of applicability for replacements for CFCs and halons as refrigerants, fire extinguishants, solvents, or foam-blowing agents. The compounds chosen are currently being synthesized by aerosol fluorination (AF), a process which is described in the paper. The actual chemical equations and experimental yields are included.

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Chlorohydrocarbons	Foam	Stationary Sources	07C	11G
Bromohydrocarbons	Aerosols	Chlorofluorocarbons		07D
Substitutes	Fluorination	Halons	14G	
Ozone		Chemical Alternatives	07B	
Refrigerants		Foam Blowing	13A	
Fire Extinguishers			13L	

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INTRODUCTION

This paper describes a research project that determines basic properties of laboratory quantities of potential alternative compounds which may be used to replace chlorofluorocarbons (CFCs) and halons listed in the "Montreal Protocol for Substances that Deplete the Ozone Layer." This research project is jointly funded by the U.S. Environmental Protection Agency (EPA) and the Electric Power Research Institute (EPRI) and is being carried out under the direction of James L. Adcock at the University of Tennessee. This project is being conducted in conjunction with a complementary effort by researchers at Clemson University. The two related but independent projects are coordinated by a Technical Advisory Group consisting of EPA and EPRI project officers, principal investigators from both projects, and other experts invited on an ad hoc basis. The authors of this paper would like to express appreciation to Powell Joyner of EPRI for technical assistance relating to this project.

Certain CFCs and halons listed in the Montreal Protocol are believed to cause depletion of the concentration of ozone found in the stratosphere. This could lead to increasing cases of skin cancer, other adverse health effects, and climate changes which may affect agriculture in the United States and throughout the world.

Since CFCs and halons are used primarily as refrigerants, foam-blowing agents, solvents, and fire extinguishants, it is necessary to search for replacements for these CFCs and halons. Promising substitutes are currently undergoing testing, including hydrogen-containing CFCs such as: HFC-134, HFC-134a, and HCFCs-123, -141b, -31, -124, and -142b. Due to the many unresolved issues associated with the leading candidates, an EPA-convened expert panel strongly recommended that research of new chemical alternatives be commenced in order to have a ready reserve of "backup" candidates in the

event that any of the primary candidates fail to meet technical, economic, toxic, energy efficient, safety, or environmental expectations.

Objectives of this cooperative agreement are to synthesize laboratory quantities of potential alternatives to determine their physical, chemical, and thermodynamic properties. The project is not intended to perform the detailed development testing that private industry undertakes in commercializing a new product but only to explore in a preliminary way possible "backup" CFC and halon alternatives for private industry to pursue as individual companies deem appropriate.

The original list of compounds from which these compounds were chosen resulted from the EPA-convened panel of fluorocarbon experts from academia and industry which met in February and April 1987 to study and recommend substitutes for additional research and development. It was felt that these compounds might possess the best combination of physical, chemical, and thermodynamic properties compared to the CFCs and halons being replaced and, at the same time, seemed likely to contribute little to either stratospheric ozone depletion or global warming.

The property testing currently posed for investigation was designed to assist in determination of applicability for the above mentioned applications. Property determinations include: normal boiling point, liquid density and vapor pressure over a range of temperatures, critical temperature and pressure, ideal gas heat capacity versus temperature, vapor density, melting point, and hydrolytic stability. Additional quantities of the potential alternatives may be synthesized later to determine atmospheric fate and acute toxicity, and for limited application tests.

The compounds chosen are currently being synthesized by aerosol fluorination (AF), a process which will be described later in this paper. The actual chemical equations and experimental yields follow. Property determinations will be the next step in this project and may be the subject of future papers.

POTENTIAL ALTERNATIVES

1. CF_3-O-CF_2CF_2H -- This compound, 2-hydryl-F-ethyl F-methyl ether, which boils below room temperature, has been prepared by the aerosol fluorination of CH_3-O-CH_2CH_2Cl producing CF_3-O-CF_2CF_2Cl which is converted to the required compound by reaction with tributyltin hydride. Overall yield is 40%.

$$CH_3OCH_2CH_2Cl \xrightarrow{\text{-----AF----}} CF_3OCF_2CF_2Cl \ 46\%$$

$$CF_3OCF_2CF_2Cl \xrightarrow[80°C/14\ hr]{Bu_3SnH/AIBN^*} CF_3OCF_2CF_2H \ 86\%$$

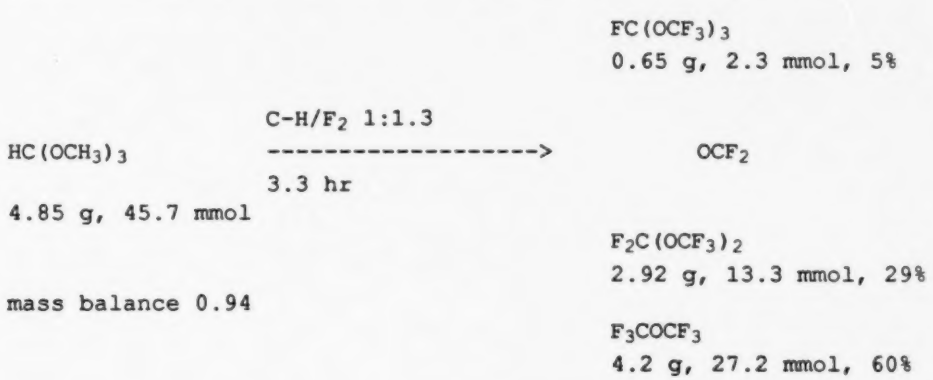
*tributyltin hydride/azobis (2-methypropionitrile)

The infrared spectrum of this compound indicates a reduced global warming potential over CFC-113 but a similarity to that of CFC-12. The ozone depletion potential of this compound is zero. The hydrogen and the ether linkage should lead to reduced atmospheric lifetimes.

2. CF_2-CF_2
   | |
   CF_2-O -- This compound, F-oxetane or F-trimethyleneoxide, has a boiling point below 0°C. It has been synthesized in 59% yield by aerosol fluorination of the analogous hydrocarbon.

With no chlorine or bromine, its ozone depletion potential is zero. It is believed that the compound will exhibit a reduced atmospheric lifetime due to the strained ether linkage. Being a perfluorocarbon it will require extensive lubricants compatibility testing. Its global warming potential is between those of CFC-12 and CFC-11.

3. CF_3-O-CF_2-O-CF_3 -- This compound, F-dimethoxymethane, has a boiling point below 0°C. It has been synthesized in 29% yield from the aerosol fluorination/beta scission of trimethylorthoformate. Other compounds formed were F-trimethylorthoformate (5%) and F-dimethyl ether (60%).



This compound has zero ozone depletion potential. With two ether linkages the compound should be photochemically sensitive and of reduced lifetime.

4. $(CF_3\text{-}O\text{-})_3CF$ -- This compound, F-trimethylorthoformate, boils at about 0°C and can be prepared in 19% yield by the fluorination/beta scission of tetramethylorthocarbonate. F-Tetramethylorthocarbonate (8%), F-dimethoxymethane (6%), and F-dimethyl ether (66%) are also isolated.

This compound has zero ozone depletion potential. With three ether linkages its atmospheric lifetime should be reduced.

5. The final group of compounds being considered are in the fluorinated dimethyl ether series from monofluoro- through hexafluorodimethyl ether (Table 1). The aerosol fluorination process is capable of controlling the relative mole ratios of dimethylether and fluorine thus controlling the degree of fluorination of the parent hydrocarbon. Superimposed upon this stoichiometric control will be a substitutional pattern which arises from the decreasing reactivity of the series: $CH_3 > CH_2F > CHF_2 >> CF_3$. As a result of this preferential reactivity, the compounds in the left-hand column are most probable, and those in the right-hand column are least probable.

TABLE 1

	MOST PROBABLE	LEAST PROBABLE
Reactant:	$CH_3\text{-}O\text{-}CH_3$	
Monofluorination:	$CFH_2\text{-}O\text{-}CH_3$	
Difluorination:	$CFH_2\text{-}O\text{-}CFH_2$	$CHF_2\text{-}O\text{-}CH_3$
Trifluorination:	$CHF_2\text{-}O\text{-}CFH_2$	$CF_3\text{-}O\text{-}CH_3$*
Tetrafluorination:	$CHF_2\text{-}O\text{-}CHF_2$	$CF_3\text{-}O\text{-}CFH_2$
Pentafluorination:	$CF_3\text{-}O\text{-}CHF_2$	
Hexafluorination:	$CF_3\text{-}O\text{-}CF_3$	

*This compound may be prepared by an alternate route.

AEROSOL FLUORINATION

Aerosol direct fluorination is a fluorination technology which produces perfluorination of functional organic molecules with only minimal fragmentation and with virtually no structural rearrangement. It is the only fluorination process which works under low acidity conditions. The basis of this technology is the fluorination of airborne particulate consisting of adsorbed organic molecules on alkali fluoride particulate. The advantage of this process is that it combines fluid processing technology with the stabilization of molecular structures in the solid phase (the aerosol particulate).

The organic-molecule-laden airborne particles are injected into a reactor which provides for the programming of fluorine concentration and temperature over its length. For perfluorination with efficient fluorine utilization, a photochemical finishing stage (which provides a steady-state, but low concentration of fluorine atoms in the reaction mixture) provides exceptional conversion of organic molecules to unrearranged/unfragmented perfluorinated organic molecules even when a stoichiometric deficit of fluorine is used. This perfluorination effect results in a bimodal product distribution when a deficit of fluorine is present, in which partially fluorinated species are similar to those produced from the reactor with the photochemical source extinguished. Partial fluorination of organic molecules can be readily achieved with fluorine substitution occurring in a predictable preferential manner. Substitution occurs step-wise with carbon radicals immobilized and capable of reacting only with gaseous fluorine. This results in exceptionally clean reactions. In fact, mixtures and components of solutions, where all components are volatile, fluorinate separately and may be separated as the analogous fluorocarbon mixture. Other aerosol generation technologies not requiring evaporation are adaptable to the process if the aerosol produced is oxygen- and water-free.

SUMMARY

This paper describes a research project that synthesizes and determines basic properties of laboratory quantities of potential alternative compounds which may be used to replace CFCs and halons listed in the "Montreal Protocol for Substances that Deplete the Ozone Layer." This project, jointly funded by the U.S. EPA and EPRI, is being carried out under the direction of James L. Adcock at the University of Tennessee.

The property testing currently posed for investigation was designed to assist in determination of applicability for replacements for CFCs and halons primarily as refrigerants, fire extinguishants, solvents, or foam-blowing agents.

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